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DEGRADATION OF SLUDGES FROM HEAVY CRUDES IN CONTAINED REACTORS

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Fate of Hydrocarbons Absorbed To Oclansorb

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EXECUTIVE SUMMARY

Oclansorb, heat-treated oil absorbent peat, commercial garden peat, Hazorb, spill absorbent and activated charcoal were compared for their ability to retain volatile hydrocarbons. Only activated charcoal effectively retained the volatile species.

Electron microscopic studies of the sorbents revealed that none contained as many surface pores as activated charcoal. Information in the literature suggests that the ability to retain volatile hydrocarbons is an adsorption phenomenon dependent on the availability and frequency of surface pores on the sorbent. This explains the inability of Oclansorb, other peat products and Hazorb to retain volatile hydrocarbons.

Because Oclansorb has an excellent ability to absorb hydrocarbons it might still be possible to construct an amalgam of Oclansorb and a highly porous material like activated charcoal to retain and prevent the release of volatiles.

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SOMMAIRE

Nous avons comparé la tourbe, Hazorb, qui absorbe l'huile, le charbon actif et Oclansorb, un produit de la tourbe qui a été chauffée.

Le microscope éléctronique a montré que le charbon actif conteint beaucoup des pores sur la surface. Les autres (Hazorb, les tourbes) ne contiennent pas autant des pores que le charbon. L'information dans les revus a suggeré que le capacité de tenir les hydrocharbons volatils dépend au nombre des pores sur le surface des materiaux absorbants. C'est pourquoi Oclansorb, Hazorb et la tourbe n'ont pas tenu les hydrocharbons volatils.

Oclansorb peut absorber l'hydrocharbon tres bien. Peutêtre c'est encore possible a construire un mélange d'Oclansorb et un matereil poreux, comme le charbon actif, pour tenir les volatiles et prévenir leur fuite.

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1.0 OBJECTIVE

To determine the fate of various hydrocarbons absorbed to Oclansorb oil absorbent peat product.

2.0 INTRODUCTION

Oclansorb, an oil absorbent heat-treated peat product, is an effective material for absorbing spilled and waste oil. It is more absorbent than many commercially available synthetic and natural absorbent products including clay and sawdust (1) and when sprinkled on spilled oil, effectively absorbs it so that the resulting oil-soaked material can be effectively disposed of (2). Oclansorb also confers the additional advantage of stimulating microbial degradation of the absorbed oil (3,4,5) perhaps by providing a support surface for oil degrading microbes, by controlling the pH of the oil degrading milieu or by stimulating the growth of these microbes. Based on these characteristics, Oclansorb has been used to effect enhanced oil degradation in a landfarm application and has been used as a solid matrix in small demonstration reactors for contained oil degradation (4,5,6).

Although Oclansorb is an effective oil absorbent, there is no data currently available on its effectiveness at retaining highly volatile materials. This is important missing information which could have consequences for the use of this product. Advantages of accelerated microbial degradation of oil in a landfarm by use of this product could be affected if volatile hydrocarbons are not controlled. Release of volatile hydrocarbons is one of the United States Environmental Protection Agency's objections to continued landfarm use for biodegradation of waste oil and oily sludges (7). Therefore, this study was performed to assess the ability of Oclansorb to retain volatile hydrocarbons.

All absorbent materials, including Oclansorb, will delay evaporation of volatile liquids. However, this experiment was designed to compare the retentive capabilities of equal weights of absorbents.

3.0 MATERIALS AND METHODS

3.1 Analytical Materials

Oclansorb oil absorbent was obtained from Hi Point Industries, Calgary AB. Samples of non heat-treated garden peat were obtained from commercial vendors. Hazorb (TM) absorbent and activated charcoal were obtained from Fisher Scientific, Fair Lawn, New Jersey.

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3.2 Electron Microscopy

A Hitachi S-2500 Scanning Electron Microscope was used for morphological examination of the surfaces. The samples were gold coated with an Edwards 150B Sputter Coater to produce a conductive surface necessary for SEM examination. Low magnification secondary electron images were obtained with 15 kV accelerating voltage and a long working distance (i.e. 30 mm) to provide the necessary depth of field. The upper secondary electron detector was used together with 25 kV accelerating voltage and a short working distance to obtain increased resolution for the high magnification images.

3.3 Gas Chromatography

Levels of toluene and dichloromethane were determined on a Hewlett Packard 5880 gas chromatograph using a 20 inch by 1/4 inch ID stainless steel column packed with 5% UCW98 on Chromasorb W. The Column was run isothermally at 85^{O} for the toluene and 50^{O} for the dichloromethane analyses. Injector and detector temperatures were 360^{O} C. The carrier gas was ultra high pure nitrogen at a flow rate of 25 mL/min. The sample of headspace gas injected was 100 microlitres.

Octane and isobutyl alcohol were analysed on a Perkin Elmer Sigma 2000 gas chromatograph equipped with an SPB-5 fused silica capillary column (30 m x 0.32 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 22 mL/min. The carrier gas was ultra high pure helium. The purge gas flow was 2 mL/min. The injector and detector temperatures were 320^{O} C. The instrument was programed to run at 50^{O} C for two minutes, then increase the temperature by 10 degrees per minute up to 100^{O}. The output of the resulting data was on an HP3390A integrator with chart speed set at 0.4 cm/min. A 50 microlitre sample of headspace gas was use for injection.

3.4 Standardization

Using toluene as a standard, a graph was generated showing the concentration of hydrocarbon vapor in the headspace of the serum vial as a function of the volume of toluene used. This was achieved by injecting varying amounts of liquid into sealed vials and measuring the concentration of hydrocarbon vapor in the headspace after one hour. Based on these data a volume of liquid hydrocarbon which resulted in complete volatilization was selected for the experiments. This

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volume was used so that hydrocarbon vapor retained by the sorbent could not be replaced by further volatilization of liquid and any decrease of hydrocarbon in the headspace would be a measure of the amount retained by the sorbent.

3.5 Procedure

Aliquots (1 - 2 microlitre) of volatile hydrocarbons (toluene, dichloromethane, octane and isobutyl alcohol) were absorbed onto varying amounts of Oclansorb, commercially available garden peat, Hazorb and charcoal in stoppered serum vials. The ratio of the hydrocarbon to Oclansorb was 1:5, 1:10 and 1:20. After equilibration for 60 minutes at 25^{O} C, the headspace gas was analysed for the presence of the particular hydrocarbon. The ratio of the headspace gas content of the hydrocarbon in presence of the Oclansorb or other absorbent to its content in the absence of absorbent was used as an index of retention of the particular hydrocarbon.

4.0 RESULTS AND DISCUSSION

4.1 Standardization

The concentration of toluene in the headspace of the serum vial as a function of the volume of liquid toluene used is shown in Figure 1. There was a linear relationship between the volume of toluene used and its concentration in the headspace up to 2 microlitres after which linearity was lost. Loss of linearity with increasing volumes of toluene is attributed to saturation of the headspace with toluene vapor. The saturation curve would have been more pronounced had there been more frequent volume increments between 2 microlitres and 5 microlitres. However, the experimental results were in agreement with calculations performed to determine the volatility of the toluene. Therefore 2 microlitres of toluene were used in the experiments performed in the presence of Oclansorb and other sorbents. Volumes of other hydrocarbons used were calculated based on their volatilities.

4.2 Hydrocarbon Retention Index

The hydrocarbon retention indices of Oclansorb, Hazorb and activated charcoal are presented in Table 1. Neither Hazorb nor Oclansorb effectively produced a reduction in the headspace hydrocarbon concentration. Partial success was obtained with octane, which, at a concentration ratio of 1:20 (octane:Oclansorb), was retained by Oclansorb by up to 28%. Commercially available garden peat also retained toluene by 18% at a concentration ratio of 1:20. While these perform

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better than Hazorb, the volume of Oclansorb or peat required to effectively retain the hydrocarbon would be impractical.

Activated charcoal retained all the hydrocarbons tested even at ratios of 1:5 and is clearly the superior material. However, its relatively high cost might make its use prohibitive also. An amalgam or pelletized product containing activated charcoal in an Oclansorb matrix may be a solution. The Oclansorb could retain the bulk of the heavier hydrocarbons and the activated charcoal could retain the volatile hydrocarbons. Charcoal-like materials have been made from peat as a cheap plentiful starting source (10, 11).

Oclansorb is a sorbent material which is slightly hydrophobic and thus absorbs hydrocarbons in preference to water. However, it does not effectively prevent their volatilization. This may be due to the physical nature of the product. Oclansorb is made from peat which is decomposed plant material. Microscopic examination of peat has revealed it to be sponge-like and highly porous with an estimated surface area of about 200 square meters per gram (12,13). In comparison, the surface area of activated charcoal is 500 - 1400 square meters per gram. Relatively high surface area makes both these materials excellent absorbents for hydrocarbons. However, scanning electron microscopic comparison of the fine structures of activated charcoal (Figure 2) and Oclansorb (Figure 3) shows that the surfaces of both are composed of small, almost circular bumps approximately 25 nm in diameter. The surface of the activated charcoal is traversed by a network of fissures up to 30 nm wide (Figure 2). This feature was absent on the Oclansorb surface (Figure 3). Fewer and smaller cracks were also present on the Hazorb surface (Figure 4). These cracks may play a role in retention of certain volatiles.

Sorbent materials work by both absorbent and adsorbent action. During absorption, the hydrocarbons are taken up by the bulk of the sorbent material while in adsorption the volatile hydrocarbons are retained at the surface of the sorbent. Adsorption can be physical and/or chemical. Physical adsorption is due mainly to physical forces of attraction including Van der Waals forces (8) while chemical adsorption encompasses ionic charge interactions between the adsorbate and the adsorbent. Adsorption of chemicals to peat will encompass these two forces depending on the nature of the material to be adsorbed. Ionic adsorption occurs in peat and ion exchange properties of peat have been known for a long time (13,14). Less understood is the method of hydrocarbon adsorption to this material which may involve hydrophobic interactions and physical forces such as van der Waals forces (8).

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Pore size coupled with surface area (i.e. the limiting volume of the adsorption space) have been reported to affect adsorption (8,12). The involvement of pore volumes in adsorption of various chemicals by Oclansorb has been demonstrated in a previous study where similar volumes of alcohols, solvents and hydrocarbons were retained by a constant weight of Oclansorb (15). However, poor retention of adsorbed volatile hydrocarbons by Oclansorb suggests it lacks effective pore space to retain the volatile hydrocarbon. This is confirmed by lack of evidence of fissures on Oclansorb under electron microscope examination unlike the surface of activated charcoal. Fissures in the charcoal particle will allow entry of the hydrocarbon deep into the sponge-like convoluted pore spaces. From here volatiles will escape slowly resulting in effective retention.

Previous studies have demonstrated that adsorption capacity for small molecules is related to the number of pores in the adsorbent and to the pore size (9). All pores were six angstroms or smaller in diameter. The electron micrographs in the present study show that Oclansorb does not contain pores even as small as 30 nm and would be unlikely to retain volatile hydrocarbons by adsorption based on pore size.

It has been suggested that pore sizes of 6 - 8 Angstroms are effective in adsorbing and separating gases (11). However, treatment of peat at high temperature has been reported to produce a carbon material with pore sizes larger than six angstroms (10,11). Improved materials with the required pore size could be obtained by addition of other materials including synthetic resins such as pheno-furfural and furyl resins to the peat before heat treatment. This has resulted in a product containing ultramicropores (10) and having improved adsorptive qualities.

5.0 CONCLUSIONS

1. Unlike activated charcoal, neither Oclansorb, Hazorb nor commercially available peat effectively retains volatile hydrocarbons.

2. Oclansorb does not contain any and Hazorb contains few small pores similar to the structures present in activated charcoal.

3. The ability to retain volatiles may be related to the number of micropores present in the sorbent matrix giving it a sponge-like texture for better retention.

4. An amalgam of Oclansorb and a highly porous carbonaceous material may be an effective sorbent to retain both volatile and non-volatile hydrocarbons.

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6.0 RECOMMENDATIONS

1. A formulation of Oclansorb and a substance like activated charcoal which retains highly volatile hydrocarbon should be assessed for improving the retention capabilities of Oclansorb.

2. The possibility of adding other materials such as pheno- furfural and furyl resins to peat before heat treatment to produce Oclansorb should be fully investigated in order to obtain a product with superior adsorption and retention properties.

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8.0 TABLES

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TABLE 1

RETENTION INDICES OF VARIOUS HYDROCARBONS BY OCLANSORB HAZORB AND ACTIVATED CHARCOAL

HYDROCARBON	CONCENTRATION*	RETENTION INDEX			
		Peat	Oclansorb	Hazorb	Activated Charcoal
Octane	1:5	-	0.98	1.01	0
	1:10	-	0.89	0.94	0
	1:20	-	0.72	0.96	0
Isobutyl alcohol	1:5	-	1.04	1.00	0
	1:10	-	1.11	1.15	0
	1:20	-	1.04	1.14	0
Toluene	1:5	-	0.94	-	0
	1:10	-	1.00	-	0
	1:20	0.82	1.06	-	0
Dichloromethane	1:5	-	0.95	0.98	0
	1:10	-	0.93	0.94	0
	1:20	-	0.83	0.91	0

* The concentration is the ratio of hydrocarbon to absorbent by weight.

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9.0 FIGURES

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FIGURE 1 TOLUENE VAPOR PRESENT IN THE HEADSPACE OF A SERUM VIAL AS A FUNCTION OF THE VOLUME OF LIQUID HYDROCARBON USED.

Increasing volumes of toluene were placed in 50 mL sealed serum vials for one hour. Then 100 microlitre samples of the headspace gas were removed and analysed by gas chromatography. The concentration of toluene in the headspace gas was plotted against the original volume of toluene placed in the serum vial.

There was a linear relationship between concentration in the headspace and the volume of toluene used up to 2 microlitres volume of toluene.

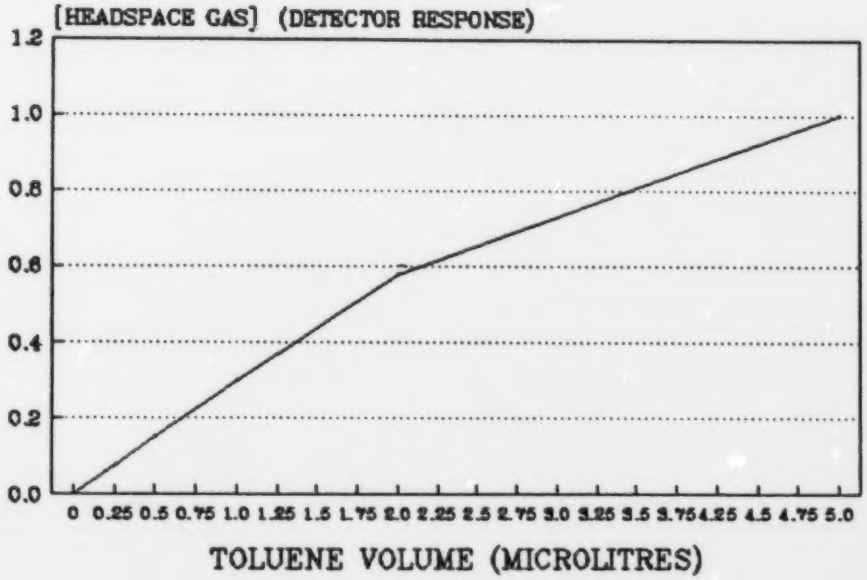

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FIGURE 2 SCANNING ELECTRON MICROGRAPHS OF ACTIVATED CARBON AT 70X AND 50,000X MAGNIFICATION

a) 70X Magnification

b) 50,000X Magnification

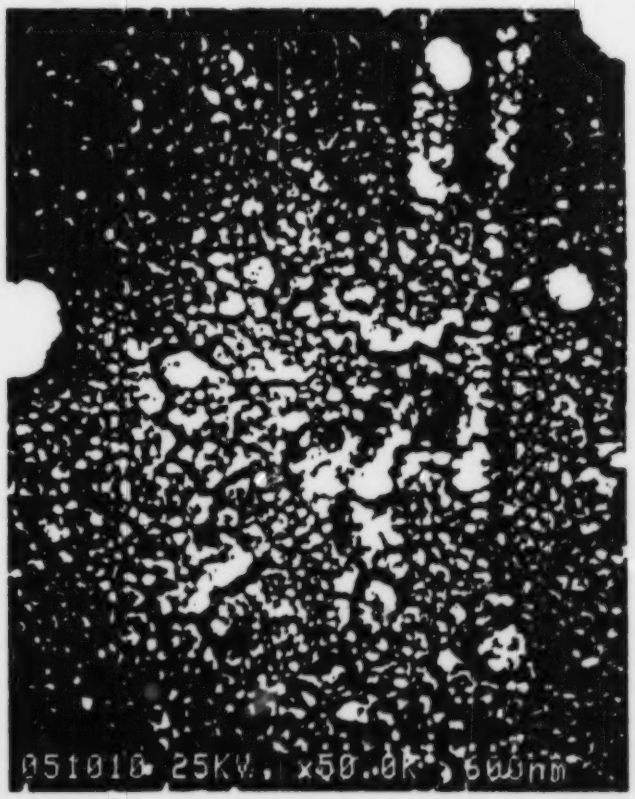

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FIGURE 3 SCANNING ELECTRON MICROGRAPHS OF OCLANSORB AT 70X AND 50,00X MAGNIFICATION

a) **70X Magnification**

b) **50,000X Magnification**

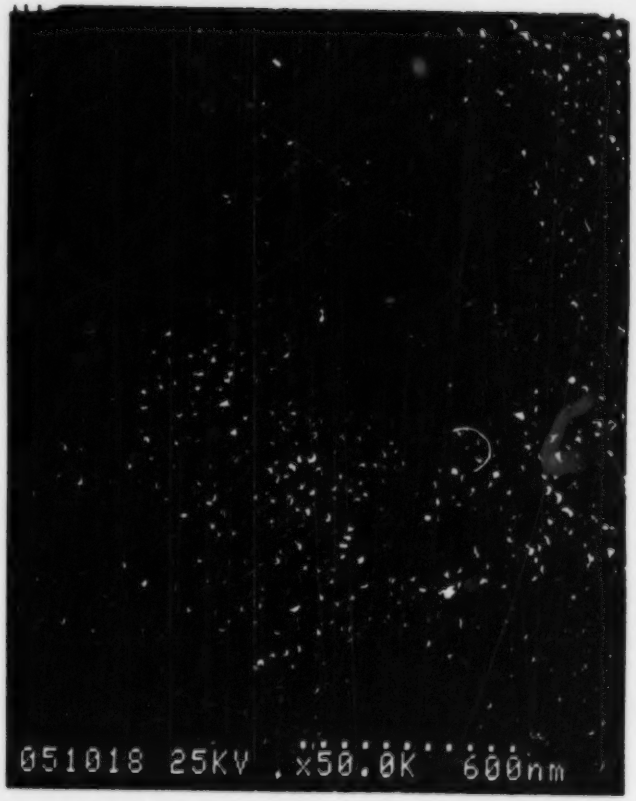

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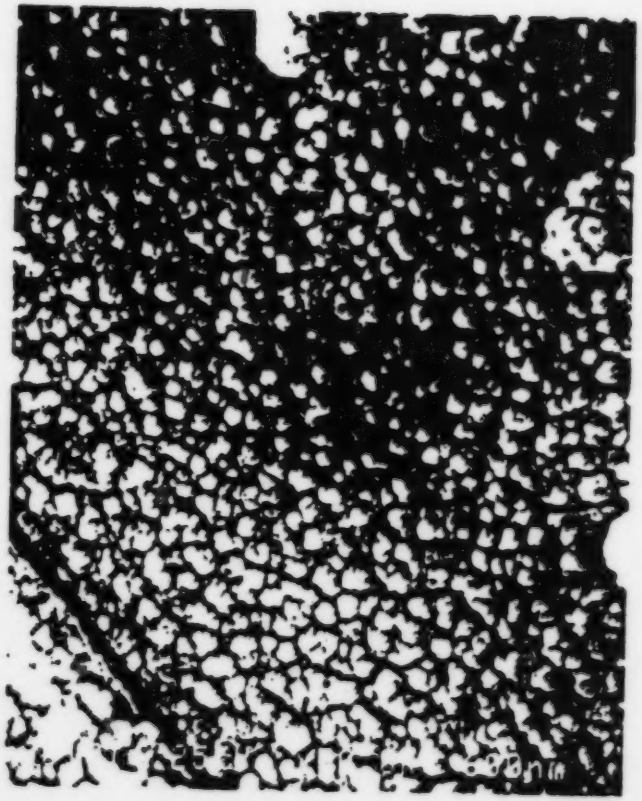
FIGURE 4 SCANNING ELECTRON MICROGRAPHS OF HAZORB AT 70X AND 50,000X MAGNIFICATION

a) **70X Magnification**

b) **50,000X Magnification**



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APPENDIX 1

Promotional Literature on Oclansorb

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OCLANSORB

soaks up
all petroleum
and
petroleum-based
fluids
on

CONTACT

OCLANSORB

WHAT IS OCLANSORB?

Oclansorb is short for ocean, land absorbent. Oclansorb is a biodegradable and non-toxic sorbent that has been developed especially for oil and oil-based chemical spills.

HOW DOES OCLANSORB WORK?

Oclansorb is a sorbent that is more effective, faster acting than most other organic and synthetic sorbents. Oclansorb has been processed to achieve maximum absorbency – oil is absorbed into the small pores or voids in Oclansorb's fibres.

WHY OCLANSORB?

- Fast acting
- Highly effective
- High oil retention
- Lightweight
- Floats
- Sorbs wide range of oil viscosities
- Organic
- Biodegradable

DATA

Material	Processed peat fibres
Sorbent to oil pickup ratio	Up to six times its weight
Effectiveness	Immediate pickup of oil and does not release
Oil Viscosities	Gasoline to oil paints and Bunker C
Application/Retrieval	Manual and/or mechanical
Shelf Life	Indefinite
Storage	Out of Rain
Toxicity	None
Package	Durable kraft paper

Product of Canada
Environmentally Safe and Non-Toxic

HI-POINT PEAT LTD.

Manufactured by Hi-Point Peat Limited, Bishop's Falls, Nfld.

WHO IS USING
OCLANSORB

OCLANSORB IS EFFECTIVE ON PCBs

Large transformers are isolated from the surrounding environment by man made dykes which often fill up with water during a rain storm. Oclansorb will remove any trace of PCBs from the water before the water is drained. Oclansorb can be used effectively to immobilize PCB contaminated oils during transportation of transformers.

HYDRO AND UTILITY COMPANIES

- Ontario Hydro
- Quebec Hydro

OCLANSORB FLOATS ON WATER

All sewage from the paper making process flows into the clarifier where solids are skimmed off. Oils leaking from the plant equipment also make their way into the clarifier but cannot be skimmed off. Oclansorb solves the problem by absorbing the oil off the water, then skimmed off with the other solids. The water is left clean before treated and returned to the environment.

PULP & PAPER COMPANIES

- Domtar
- CIP Gatineau
- Dominion Cellulose
- Les Industries McLaren

OCLANSORB IS EASILY DISPOSED OF

Oils and oil based chemicals are often spilled during the manufacturing process, while handling and transporting. To clean up these spills efficiently and economically, Oclansorb is used more frequently as the product can be disposed of by incineration or by landfilling. Incineration or land filling would only be recommended if local, provincial and federal regulatory officials have given approval.

OIL REFINERIES, PETROCHEMICAL AND CHEMICAL PLANTS

- Petro Canada
- Shell Canada
- Esso
- Sunoco
- Texaco
- Ultramar
- Ashland Chemicals
- PolySar
- Stan Chem-Cil
- Van Waters & Rogers
- Cilco Maintenance

OCLANSORB IS NON-ABRASIVE

Jet fuel is always spilled onto the tarmac when jets are being refueled. Clay is predominately used to clean up these spills because of the low cost. However, clay is abrasive and can cause damage if sucked into jet engines. Oclansorb is organic and non-abrasive and is being widely accepted as a replacement for clay.

AIRPORTS

- Dorval
- Mirabel
- Quebec Municipal
- Pearson International
- Calgary International
- Watson Lake - Yukon

OCLANSORB ABSORBS ON CONTACT

When gasoline or other petroleum based liquids are spilled on highways or city streets, the fire department is called in immediately to clean up a potentially hazardous situation. Gasoline can make its way into storm sewers forcing evacuation of homes and businesses. Oclansorb absorbs on contact. Once absorbed Oclansorb does not release the gasoline.

FIRE DEPARTMENTS

- Ottawa
- Nepean
- Kingston
- New Market

OCLANSORB IS ECONOMICAL

Railway and transportation companies have large yards for maintenance and storage of engines, rail cars, trucks, etc. The amount of petroleum spills is numerous and the size of spills vary. To keep down the cost of cleaning spills, Oclansorb has proven the cost per clean up is less because the amount and time needed is less than other petroleum sorbents.

RAILYARDS, TRANSPORTATION YARDS

- Canadian National
- Transport Canada

Product of Canada
Environmentally Safe and Non-Toxic

HI-POINT PEAT LTD.

Manufactured by Hi-Point Peat Limited, Bishop's Falls, Nfld.